SUBJECT - CHEMISTRY

CLASS - B.Sc(Hons) PART- III

PAPER - V

TOPIC - Duhem-Mergules equation

Dr Hari Mohan prasad Singh
Department of Chemistry
Dr. L.K.V. D College Tajpur Samastipur

Q Deduce Duhem-Mergules equation.

Ans. Duhem-Mergules equation: The Gibbs-Duhem equation is given by

$$\Sigma n_i dM_i = 0$$

for a system consisting of a liquid solution of two components 1 & 2 in equilibrium with their vapours at constant temperature and pressure, The condition for infinitesimal change of composition is given by -

$$n_1 dM_1 + n_2 dM_2 = 0$$

$$\text{or } n_1 dM_1 = n_2 dM_2 \quad \text{---} \quad (1)$$

Where n_1 & n_2 are the number of moles of components 1 & 2 respectively in a given mixture Dividing both sides by (n_1+n_2), we get -

$$\frac{n_1}{n_1+n_2} dM_1 = -\frac{n_2}{n_1+n_2} dM_2$$

$$\text{or } X_1 dM_1 = -X_2 dM_2 \quad \text{---} \quad (2)$$

where X_1 & X_2 are respective mole fractions. Now in the mixture (1) & (2)

$$X_1 = (1 - X_2) \quad \therefore \quad dX_1 = -dX_2$$

$$\therefore X_1 \frac{dM_1}{dX_1} = X_2 \frac{dM_2}{dX_1} = X_2 \frac{dM_2}{dX_2} \quad \text{---} \quad (3)$$

In a liquid mixture, the chemical potential of a particular constituent is given by

$$\mu_i = \mu^0 + RT \ln P_i$$

where P_i is partial vapour pressure of ith constituent assuming the vapour to behave as an ideal gas. Applying the equation to components 1 & 2 and differentiating w.r to x_1 & x_2 at constant temperature and pressure, we get

$$\frac{d\mu_1}{dx_1} = RT \frac{d \ln P_1}{dx_1} \quad \& \quad \frac{d\mu_2}{dx_2} = RT \frac{d \ln P_2}{dx_2} \quad \cdots (4)$$

Combining eq (3) and (4) we get -

$$x_1 \frac{d \ln P_1}{dx_1} = x_2 \frac{d \ln P_2}{dx_2}$$

$$\text{or} \quad \frac{d \ln P_1}{d \ln x_1} = \frac{d \ln P_2}{d \ln x_2} \quad \cdots (5)$$

This is Duhem-Margules equation showing relationship between the proportion of constituents in the mixture and their partial vapour pressures.